



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the manufacture of Pigment Preparations

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

There are very many kinds of substratum that are advantageously coloured with pigments, that is to say, colorants that are not only insoluble in water but also in various organic solvents or that are, for all practical purposes, insoluble in organic solvents. It is this property that prevents subsequent migration or even bleeding of the colorants. It is often difficult, however, to disperse a pigment powder finely and uniformly in a given substratum. To overcome this difficulty, it is often the practice to make use of pigment preparations in which a pigment in concentrated form is dispersed in a suitable carrier material. Such pigment preparations must, of course, possess a number of specific properties if they are to fulfil their purpose. For example, the pigment must be uniformly dispersed in the preparation, and the carrier material used must be chosen to suit the task in hand, that is to say, it must be compatible with the substratum ultimately to be coloured and it must be possible to effect its incorporation in the said substratum without difficulty.

It is often the practice to work the pigment into the carrier material by a kneading or rolling process, and it is possible to achieve adequate dispersion of the pigment in the carrier material of the pigment preparation by such a process, especially when the operation is carried out for a sufficiently long period of time. However, there are still many carrier materials that exhibit unsatisfactory behaviour in this respect.

As a result of the increasing importance of polyolefines in the plastics field, especially polyethylene and polypropylene, a need has arisen for pigment preparations that are compatible with the said synthetic materials. The idea suggested itself that the polyolefines themselves be used as carriers for such pigment preparations, but such preparations have not proved entirely satisfactory.

The present invention is based on the observation that better results in various respects can be obtained when pigment preparations are made by grinding a pigment together with a polyethylene wax or polypropylene wax as carrier material and water in a comminuting device provided with solid grinding members.

All the polyethylene waxes that are available commercially under a variety of trade-names and that are normally obtained by pyrolysis from high molecular weight polyethylene may be used.

The polypropylene waxes that may be used as carrier substances in the process of the present invention are obtained, for example, by heating isotactic polypropylene to a temperature between about 250 and 400°C., for example, by heating for at least 15 minutes at about 350 to 400°C. or for about 30 to 120 minutes at lower temperatures within the range indicated. Heating may be effected with or without the exclusion of atmospheric oxygen. Preferably a polypropylene wax having a melting point in the range of 110°C. to 150°C. is used.

The properties of the polypropylene waxes are entirely different from those of the isotactic polypropylenes from which they are obtained. For example, melts prepared from the waxes display a much lower viscosity, and the solid products have a lower degree of hardness.

Notwithstanding the considerable chemical and physical differences between the starting material and the waxes, the latter are highly compatible with isotactic polypropylene.

5 The known inorganic and organic pigments may be used in the process of the invention. Examples of inorganic pigments are, in particular, titanium oxide, the iron
oxides, cadmium pigments and the various kinds of carbon black, for example, lamp
black and gas black. Organic pigments that may be mentioned are, in particular, azo
10 pigments, for example, pigments containing two azo groups in the molecule. It is
also possible to use many anthraquinone pigments, including some proper vat dye-
stuffs, as well as the known chlorinated and non-chlorinated phthalocyanine colorants.
Also suitable are pigments of the dioxazine, quinacridone, indigoid, perylene - tetra-
carboxylic diimide and perinone series. The quantitative ratio of pigment to poly-
ethylene wax or polypropylene wax is advantageously such that the proportion of pig-
ment in the finished preparation is 25 to 75% by weight. The lower limit is not
15 critical since too low a pigment content would be uneconomical, whereas too high
a pigment content is frequently associated with deterioration of the pigment dispersion.
Accordingly, a pigment content of 60 to 65% should not be exceeded, depending on
the degree of dispersion required.

20 If desired, mixtures of different pigments may be used in the process of the invention instead of a single pigment or mixtures of different waxes instead of a polyethylene or polypropylene wax.

The manufacturing process, namely, grinding in aqueous suspension, is very simple
to carry out. It can be performed in conventional ball or roller mills, as desired. It is
advantageous, however, to use mills in which grinding elements for example glass
25 balls, porcelain balls or similar balls, or hard pebbles are agitated by means of a
suitable stirring device. The factor which such comminuting devices have in common
is that the grinding elements can move relatively freely and exert both a rubbing and
pounding action.

30 It is important that the present process be carried out in aqueous suspension. This has the advantage, for example, that pigment presscakes moist with water may
be used because in many manufacturing processes such presscakes are directly
obtained. If it is desired to use the pigment in dry form an aqueous suspension of the
pigment is obtained as soon as the comminuting device begins to work. The procedure
is, for example, to introduce the requisite amounts of pigment and polyolefine wax
35 into the grinding device, and then to add at least about twice the amount of water,
based on the solid material. The amount of water used is not critical and may be, for
example, up to 20 times the amount of solid substance.

The sequence in which the ingredients are added to the grinding device is not
critical; in certain circumstances, for example, it may be advantageous to add the
40 water first and the solid material afterwards. The polyethylene or polypropylene wax
is advantageously added in powder form. The size of the powder particles is not
critical, but it is advantageous for them to be substantially smaller than the grinding
elements.

45 The use of water as liquid grinding medium has a further advantage in that there is no fire hazard, which is not the case with non-aqueous organic liquids. Small
amounts of organic liquids, especially those having a relatively powerful wetting action,
for example, sparingly water-soluble alcohols, for example, amylalcohol, may be added
with advantage in some cases. However, the amount added must be extremely small—
only a small percentage, based on the amount of water used. It is also possible to
50 add conventional cationic, anionic or non-ionic wetting agents. It is not necessary
to use a large amount of wetting agent in this process as is frequently the case in
aqueous grinding operations; it can, in fact, be troublesome. It is advantageous to cool
the grinding device during the grinding operation.

55 In the wet grinding process described above, in which water is used as liquid grinding medium, the pigment is comminuted in the normal manner and it also
migrates into the wax.

On completion of the grinding process, the duration of which naturally depends
on the particle size required, the particle size of the pigment prior to the operation,
and other factors, the preparation may be worked up in a simple manner. The aqueous
60 suspension is filtered, the filter residue is washed with water and then dried care-
fully, for example, in a vacuum cabinet.

The preparations obtained by the process of the present invention may be used
for a very wide variety of purposes in all cases where the polyethylene or poly-
propylene wax is sufficiently compatible with the substratum to be coloured. For

example, they may be used for colouring compositions to be used in injection moulding processes, which compositions consist mainly of polyethylene or polypropylene. However, they may also be used, for example, for colouring plasticised polyvinyl chloride and rubber, and are especially suitable for processes in which the material is not machined, for example, the injection moulding process.

Since the pigments used can be reduced to a very fine particle size, the preparations obtained by the process of the invention may also be used for the spin-coloration of polyethylene or polypropylene fibres.

Compared with the kneading method mentioned above for the preparation of such pigment preparations, the process of the invention ensures better dispersion of the pigment in the carrier material, and this, in turn, ensures a better colour yield. The use of waxes instead of the high molecular weight polyolefines themselves has various advantages; for example, they are easy to work into the composition to be coloured, and facilitate very fine dispersion of the pigments.

The preparation of polypropylene waxes that are, for example, suitable for use in the present process is described hereinafter. The manufacture of the pigment preparations is described in the Examples.

I Preparation without the exclusion of atmospheric oxygen

Isotactic high molecular weight polypropylene which is insoluble in *n*-heptane to 94.4% and which has a melting point of about 165°C., measured on a Kofler hot plate, is used as starting material. The polypropylene is melted and kept at 330°C. for 30 minutes. The melt, which now has a low viscosity, is allowed to cool while stirring, and a wax-like granulate is obtained. This is ground in a hammer mill with the addition of dry ice (solidified carbon dioxide). The material is sieved through a 0.5 mm sieve, and the powder obtained has a slight brownish tinge and melts at about 138°C.

II Preparation in a nitrogen atmosphere

a) The polypropylene mentioned above is maintained at 300°C. for 30 minutes. After processing in the manner described above, the wax has a melting point of about 149°C.

b) The above-mentioned polypropylene is maintained at 300°C. for 90 minutes; the wax obtained has a melting point of about 141°C.

c) The above-mentioned polypropylene is maintained at 350°C. for 30 minutes; the wax obtained has a melting point of about 128°C.

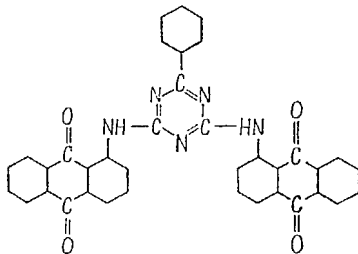
d) The above-mentioned polypropylene is maintained at 400°C. for 20 minutes; the wax obtained has a melting point of about 112°C.

All the above-mentioned polypropylene waxes are suitable for the manufacture of pigment preparations by the process of the invention. It is also possible to replace a small proportion of the polypropylene wax by polyethylene or polypropylene.

The following Examples illustrate the invention. Unless otherwise stated, the parts and percentages are by weight.

EXAMPLE 1.

A mixture comprising 10 parts of the polypropylene wax obtained by Process I, 10 parts of a yellow pigment of the formula



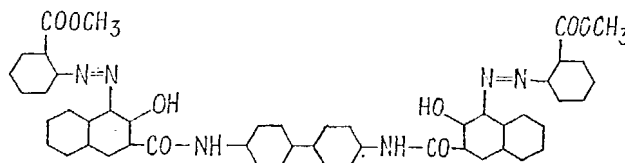
[1-phenyl-3:5-di(1'-anthraquinonylamino)triazine]

and 120 parts of water is ground in an attrition mill for 12 hours. The ground material, together with the water used to wash out the grinding apparatus, is then transferred to a suction filter. It is then filtered, the filter residue is given a brief wash with water, and the filter cake is then dried in a vacuum cabinet at 90°C. The

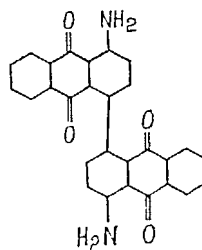
dried material is sieved through a sieve having a mesh size of 1 mm. i.e. having holes each of 1 sq. mm.

The product may be used for the mass-coloration of polypropylene. 0.05 part of the preparation is admixed with 100 parts of polypropylene granules, and the mixture is extruded once at 240°C. A transparent, homogeneously coloured yellow strip is obtained that contains the coloured pigment in a state of fine and uniform dispersion.

Equally good results are obtained in respect of homogenous and fine dispersion of the pigment preparation by the above method when the following pigments are used instead of the yellow pigment: the red azo pigment of the formula

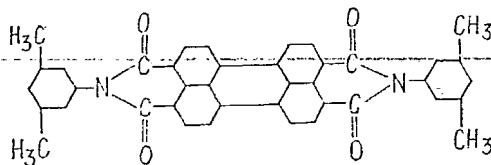


the red pigment of the formula



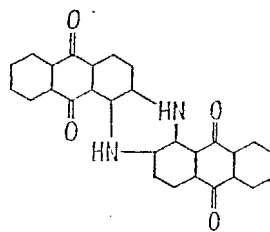
(4:4'-diamino-1:1'-dianthraquinonyl)

the red pigment of the formula



[perylene-tetracarboxylic acid-di-(3':5'-dimethylphenylamide)]

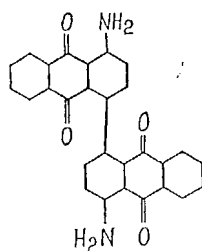
and the blue pigment of the formula



(indanthrone)

EXAMPLE 2.

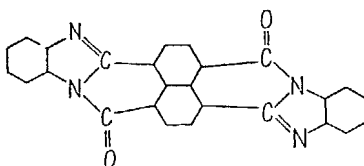
A mixture comprising 10 parts of the polypropylene wax obtained by Process I, 10 parts of the above-mentioned red pigment of the formula



and 120 parts of water is ground in an attrition mill for 12 hours. The ground material is suction-filtered, washed with water and then dried in a vacuum cabinet at 90°C. The dried material is then sieved through a 1 mm sieve to yield a soft-grained powder which may be used to colour plasticised polyvinyl chloride, for example, as follows:

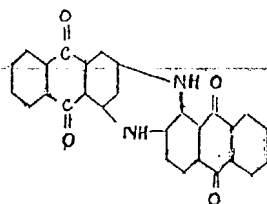
0.08 part of the above pigment preparation, 13.3 parts of polyvinyl chloride and 7.2 parts of dioctyl phthalate are mixed for 5 minutes at 150°C. on a two-roller mill. The transparent foil obtained at the end of this operation is coloured an intense red-blue and contains the colorant in a state of very fine and uniform dispersion.

Similar or identical results in respect of homogeneous and fine dispersion of the pigment in the pigment preparation are obtained when the following pigments are used instead of the red pigment: the orange pigment of the formula



and the blue pigment of the formula

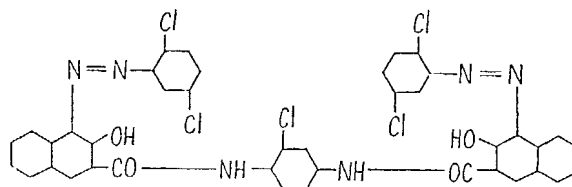
trans-form



(indanthrone)

EXAMPLE 3.

A mixture comprising 10 parts of polypropylene wax obtained by Process I, 10 parts of a red azo pigment of the formula

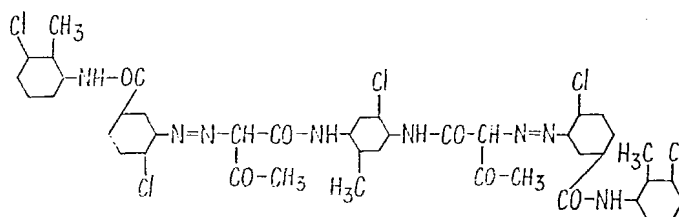


and 120 parts of water is ground in an attrition mill for 12 hours. The ground material is suction-filtered, washed with water and then dried in a vacuum cabinet at 90°C. The dried material is sieved through a 1 mm sieve to yield a soft-grained powder which is suitable for the mass coloration of polyethylene. Coloration may be carried out as follows:

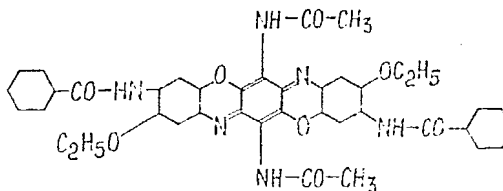
0.04 part of the above preparation and 20 parts of low-pressure polyethylene are worked to and fro for 5 minutes at 160°C. on a two-roller mill. A transparent, red foil is obtained that contains the pigment in a very fine and homogeneous state of dispersion.

Pigment preparations having similar or identical properties in respect of homogeneous and fine dispersion in the application medium are obtained when using the following pigments instead of the red pigment:

β -copper phthalocyanine,
4:4'-7:7'-tetrachlorothioindigo,
 α -quinacridone,
the yellow azo pigment of the formula



and the violet dioxazine pigment of the formula



EXAMPLE 4.

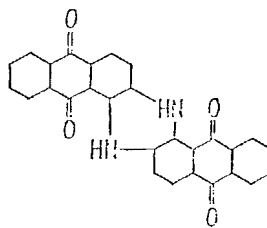
A mixture comprising 10 parts of the polypropylene wax obtained by Process I, 10 parts of green polychloro-copper phthalocyanine, 2 parts of amyl alcohol and 118 parts of water is ground in an attrition mill for 12 hours. The ground material is suction filtered, washed with water and dried in a vacuum cabinet at 90°C. Sieving through a 1 mm sieve yields a soft-grained powder. The preparation thus obtained may be used for the mass coloration of polyethylene, the procedure being as follows:

0.04 part of the preparation and 20 parts of low-pressure polyethylene are worked to and fro for 5 minutes at 160°C. on a two-roller mill. A transparent foil coloured a homogeneous green is obtained which contains the pigment in a state of very fine dispersion.

When using 2 parts of *n*-butyl alcohol instead of amyl alcohol, but otherwise proceeding in the same manner, a very similar result is obtained when the pigment preparation is used to colour low-pressure polyethylene.

EXAMPLE 5.

A mixture comprising 10 parts of the finely pulverised blue dyestuff of the formula



(indanthrone)

10 parts of finely pulverised polypropylene wax obtained by Process I and 120 parts of water is ground in an attrition mill for 12 hours. The ground material is

suction filtered, given a brief wash with water and then dried in a vacuum cabinet at 85°C. The dried material is then sieved through a 1 mm sieve and used for the mass coloration of polyethylene, the procedure being as follows:

5 0.04 part of the above preparation and 20 parts of low-pressure polyethylene are worked to and fro for 5 minutes at 150°C. on a two-roller mill. A transparent, blue foil is obtained that contains the colorant in a state of very fine and homogeneous dispersion. 5

10 Identical or very similar colorations are obtained when polypropylene waxes produced in a nitrogen atmosphere, for example, by Processes IIa or IIc, are used instead of the above polypropylene wax. These waxes are likewise used in powder form, the powder being obtained by grinding in the presence of dry ice and sieving through a 0.5 mm sieve. 10

EXAMPLE 6.

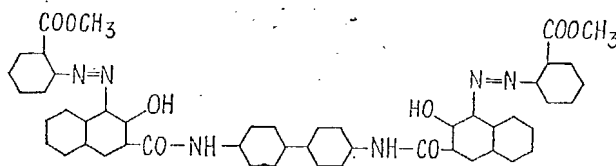
15 A mixture comprising 8 parts of lamp black, 12 parts of pulverised polypropylene wax obtained by Process I and 120 parts of water is ground in an attrition mill in the manner described in the preceding Examples. 15

20 0.05 part of the preparation thus obtained and 20 parts of low-pressure polyethylene are worked to and fro for 5 minutes at 150°C. on a two-roller mill. A black foil is obtained which contains the pigment in a state of very fine and homogeneous dispersion. 20

A mixture comprising 14 parts of titanium dioxide (rutile), 6 parts of the polypropylene wax obtained by Process I and 120 parts of water are ground in the same manner. When 0.03 part of the pigment preparation thus obtained is worked into 20 parts of low-pressure polyethylene, a foil of homogeneous white is obtained.

EXAMPLE 7. 25

A mixture comprising 10 parts of the polypropylene wax obtained by Process I, 10 parts of a finely ground red azo pigment of the formula



30 and 120 parts of water is ground in an attrition mill for 12 hours while cooling with water. The ground material is suction filtered, given a brief wash with water and dried in a vacuum cabinet at 85°C. The dried material may then be used as follows for the mass coloration of polyethylene: 30

35 0.04 part of the pigment preparation, 20 parts of low-pressure polyethylene and 1 part of titanium dioxide (rutile) are worked to and fro for 5 minutes at 150°C. on a two-roller mill. A red foil is obtained that contains the pigment in a state of fine and homogeneous dispersion. 35

40 When the above aqueous grinding process is carried out in the manner described above, but with the addition of 0.1 or 0.5 part of the sodium salt of a dispersing agent obtained by condensing naphthalene- β -sulphonic acid and formaldehyde, and the preparation obtained is worked into low-pressure polyethylene, a foil is obtained that contains the pigment in a state of very fine and uniform dispersion, the coloration being identical in strength to somewhat stronger. 40

EXAMPLE 8.

45 A pigment preparation is made in the manner described in Example 7 by grinding a mixture comprising 10 parts of the red pigment, 10 parts of polypropylene wax and 120 parts of water. 45

50 0.08 part of the preparation thus obtained, 13.3 parts of polyvinyl chloride, 7.2 parts of dioctyl phthalate and 1 part of titanium dioxide (rutile) are worked to and fro for 5 minutes at 150°C. on a two-roller mill. A red foil is obtained that contains the pigment in a state of very fine and uniform dispersion. 50

Preparations producing identical or very similar colorations in plasticised polyvinyl chloride are obtained when the above aqueous grinding operation is carried out

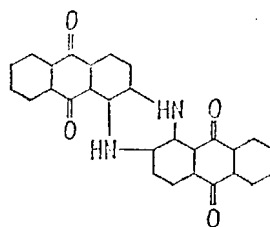
with the addition of 10 parts of isopropyl alcohol or 0.4 part of lauryl alcohol or 0.1 part of the reaction product of 15 mols of ethylene oxide and 1 mol of cetyl alcohol or 0.4 part of a 30% aqueous solution of the hydrochloride of mono-oleyldiethyl-ethylenediamine.

EXAMPLE 9.

A mixture comprising 34.3 parts of a presscake of polychloro-copper phthalocyanine having a dry content of 29.2%, 10 parts of the polypropylene wax obtained by Process I and 96 parts of water is ground in an attrition mill for 12 hours while cooling with water. The ground material is suction filtered, given a brief wash with water and then dried in a vacuum cabinet at 85°C. The product can be used for colouring plasticised polyvinyl chloride by the process described in Example 8. A green foil is obtained that contains the pigment in a state of very fine and uniform dispersion. Preparations producing identical or very similar colorations in plasticised polyvinyl chloride are obtained when the above aqueous grinding process is carried out with the addition of 2 parts or 5 parts of amyl alcohol.

EXAMPLE 10.

A mixture comprising 10 parts of the polyethylene wax "A—C Polyethylene 629" (a product of Allied Chemicals, U.S.A.) melting at approximately 103°C., 10 parts of a blue pigment of the formula



(indanthrone)

and 120 parts of water is ground in an attrition mill for 12 hours. The ground material is suction filtered, washed with water and dried in a vacuum cabinet at 90°C. It is sieved through a 1 mm sieve and a soft-grained blue powder is obtained. The preparation can be used for the mass coloration of polyethylene. 0.04 part of the preparation and 20 parts of low-pressure polyethylene are worked to and fro for 5 minutes at 160°C. on a two-roller mill. A transparent foil of a homogeneous blue is obtained that contains the pigment in a state of fine dispersion.

Identical results are obtained with Epolene N—10 produced by Eastman Kodak; its softening point is 111°C. and it has a density of 0.93. "Epolene" is a registered Trade Mark.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a pigment preparation, wherein a pigment, a polyethylene wax or polypropylene wax as carrier material and water are ground in a comminuting device provided with solid grinding members.

2. A process as claimed in Claim 1, wherein a comminuting device is used in which the grinding elements are agitated by a stirrer.

3. A process as claimed in Claim 1 or Claim 2, wherein a polypropylene wax having a melting point in the range 110°C. to 150°C. is used.

4. A process as claimed in Claim 3, wherein the polypropylene wax is obtained by heating isotactic polypropylene.

5. A process as claimed in any one of Claims 1 to 4 wherein the quantitative ratio of pigment to polyethylene wax or polypropylene wax is such that the proportion of pigment in the finished preparation is 25 to 75% by weight.

6. A process for the manufacture of pigment preparations as claimed in Claim 1 conducted substantially as described herein.

7. A process as claimed in Claim 1, conducted substantially as described in any one of the Examples herein.

8. Pigment preparations whenever obtained by the process claimed in any one of Claims 1 to 7.

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court,
Chancery Lane, London, W.C.2.

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